POWER GENERATION AND GASEOUS EMISSIONS PERFORMANCE OF AN INTERNAL COMBUSTION ENGINE FED WITH BLENDS OF SOYBEAN AND BEEF TALLOW BIODIESEL

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Abstract

This study aimed to compare the performance of an internal combustion engine fed with blends of biodiesel produced from soybean and diesel, and blends of biodiesel produced from beef tallow and diesel. Performance was evaluated in terms of power generated at low loading conditions (0.5; 1.0 and 1.5 kW) and emission of organic and inorganic pollutants. In order to analyze inorganic gases (CO, SO_2 and NO_x), an automatic analyzer was used and the organic emissions (BTEX) were carried out using a Gas Chromatograph (GC). The results indicate that the introduction of the two biodiesels in the fuel caused a reduction in CO, SO_2 and BTEX emissions. In addition, the reduction was proportional to the increase in loading regime. Beef tallow biodiesels presented better results regarding emission than soybean biodiesels. The use of pure biodiesels also presented a net reduction in pollutant gas emissions without hindering the engine generator performance.

Key-words: air pollution; biodiesel; diesel; gas emissions; volatile organic compounds.

1. Introduction

The development of alternative – and cleaner - sources of energy has become a major preoccupation of researchers and businesses alike. In particular, the use of biodiesel as an energy source is becoming a viable and environmentally friendly alternative to diesel. Several studies reported in the literature suggest the environmental advantages of using biodiesel – pure or in blends with diesel - for internal combustion engines. A study carried out by the U.S. EPA [1], estimated that the use of a blend with 20% soybean-generated biodiesel and 80% diesel leads to a reduction of ~10% in particulate material, ~21% in hydrocarbons and 11% in carbon monoxide emissions, but a 2% increase in NO_x emissions. Ferreira et al. [2] analyzed the volatile organic compound (VOC) emissions in compression ignition engines fueled with diesel and a blend of diesel and biodiesel (B10). In their study, an indirect-injection, four-cylinder engine, coupled with a hydraulic dynamometer, was used with a maximum power generation of 50 kW. The engine worked for 30 hours under varying torques and at a constant rotation (2500 rpm). The results showed a reduction in benzene (19.5%) and ethylbenzene (4.2%) emission with the use of B10, in comparison to pure diesel emissions. Corrêa and Arbilla [3] tested mamona ethyl-derived biodiesel in a six-cylinder diesel engine, at 1500 rpm rotation and steady-state. They obtained a reduction in monoaromatic and polyaromatic hydrocarbon emissions when biodiesel was added to the fuel mix. Dorado et al. [4] carried out tests with pure waste olive oil methyl ester-derived biodiesel and diesel in indirect injection engines operating under steady-state. In this situation, it was verified that the use of biodiesel led to a reduction in CO (~59%); CO_2 (~9%); NO (~37%) and SO_2 (~58%) emissions. However, the introduction of these types of biodiesel caused an 81% increase in NO_2 emissions and 8.5% increase in fuel consumption. In addition, the technical literature in this particular field seems to corroborate the statement that biodiesel combustion emissions are directly dependent on raw-material precursor and engine operation conditions, such as load and power.

The purpose of this study was to evaluate the emissions of inorganic (CO, NO_x and SO_2), and organic (benzene, toluene, ethylzenbene and xylene – BTEX) pollutants, as well as the energetic performance of an internal combustion engine operating under low loadings. Due to their toxicity and harmful effects to human health even in low concentrations, the organic compounds chosen for quantification were benzene, toluene, ethylbenzene and xylenes (BTEX) [5]. They are mainly released by vehicles and are amongst the most commonly found volatiles in the urban atmosphere [5-7]. They are considered as precursors of photochemical reactions that occur in the lower atmosphere, contributing to the formation of photochemical smog [8].

The fuels used were blends of soybean biodiesel and mineral diesel, and blends of the latter with beef tallow biodiesel and mineral diesel. Several volumetric blending proportions with mineral diesel were used (B0, B5, B20, B50 and B100). Beef tallow and soybean are by far the main precursors of biodiesels in Brazil, corresponding to ~92% of the biodiesel production in the country [9].

A great number of studies involving biofuels are restricted to their possible use as a substitute for gasoline and diesel, and how the latter two compare with biofuels in terms of energy output. Quite often, environmental aspects associated with fuel use, such as quantities of greenhouse emissions, are not considered. This aspect is considered herein and is one important novelty of the study.

2. Material and methods

2.1 Diesel, biodiesel and blends

In order to carry out the tests in a bench engine, pure type A diesel (provided by Petrobras S.A., Brazil) was used. It had a maximum sulfur content of 1800 ppm and was exempt of any additives. The two basic biodiesel fuels, soybean methyl ester biofuel (herein identified as SB) and beef tallow biofuel (herein identified as BT), were obtained from companies registered at the Petroleum Natural Gas and Biofuels National Agency (ANP, Brazil). BT is a mix of beef tallow methyl ester (62%) and soybean methyl ester (38%). The BT composition results from regulatory requirements that state that soybean must be added to beef tallow so that BT meets the ANP requirements [10] to be commercialized as fuel [11].

The upper heating value (UHV) was determined in the laboratory for the three fuels and their blends. The lower heating value (LHV) for each fuel and composition tested was estimated according to Penido Filho [12]. Blends were prepared with 0, 5, 20, 50 and 100% vol. of each biodiesel in the diesel. These proportions are represented herein by B0, B5, B20, B50 and

B100. Formulation B5 was required by Brazilian legislation when the experiments were performed [13]. As of 2015, the required proportion is 7%.

2.2 Characterization of the engine used and performance tests

Emission and power-generation performance tests were performed with a direct-injection, monophase power generator (Branco, model BD 6500 CF) yielding 7.36 kW of power coupled with a 5.5 kW load panel. For each diesel-biodiesel proportion (SB0 to SB100 and BT0 to BT100), the following loadings were evaluated: 0.5 kW, 1.0 kW and 1.5 kW, corresponding to approximately 10%, 20% and 30% of the total load supported by the load panel (5.5 kW). It is worth noting that the manufacturer claims that this Branco model can be powered by alternative fuels (such as biodiesel).

Engine performance evaluations were carried out for each blend of fuel. The first step was to calculate the brake specific fuel consumption (BSFC; g/kWh) using mass consumption data (kg/s) and applying Eq. (1):

$$BSFC = {}^{3600\,MC}/_{Vi} \qquad (1)$$

where V is the output voltage (V) and i is the electrical current (A)

Finally, the overall performance, expressed as overall efficiency as a function of the system load (E; %), was calculated using Eq. (2) [14]:

$$E = \frac{3600}{\text{LHV BSFC}} \times 100 \qquad (2)$$

All the necessary parameters were collected in duplicate and the statistical analysis used was the Randomized Experimental Block Design (Tukey test, at 5% probability level).

2.3 Combustion emission tests

2.3.1 Inorganic gases

An automatic combustion gas analyzer (Bacharach, model PCA3-285KIT / 24-8453) was used to monitor the emissions of CO, NO_x ($NO+NO_2$) and SO_2, which are typically released by diesel cycle vehicles. The equipment probe was located near the exhaust gas outlet (or pipe), transversally to the combustion gas exhaust flow. For each sampling, the analyzer was brought to equilibrium with the environmental conditions until the oxygen measurement leveled back to 20.9% vol. at atmospheric pressure. Inorganic gas emissions were assessed for loads 0.5, 1.0, and 1.5 kW, using the same number of fuel formulations previously described. More than 50 samples were collected for CO analysis and 30 for SO_2 and NO_x for each fuel blend. Statistical analyses were performed following the Randomized Experimental Block Design Test (Tukey test, at 5% probability level).

2.3.2 Organic gases

Sampling and analyses

Organic emission tests were carried out for all fuel blends and power loadings. Organic gas sampling followed the U.S. EPA Compendium Method TO-17 [15]. The VOC present in the air were collected by active sampling onto 89-mm long, 6-mm OD and 4-mm ID Perkin Elmer glass sorbent tubes. The solid adsorbent used was the 60-80 mesh, 35-m^2/g specific surface area porous polymer Tenax TA (2,6-diphenyl-p-phenylene oxide; supplied by Supelco). The sorbent tubes were filled with 180 mg Tenax TA and conditioned in automatic thermal desorption for 30 minutes at 320 ºC. This ensured the removal of any artifact that could be present in the adsorbent bed. The choice for this adsorbent took into account its hydrophilic feature, minimum artifact level (<1 ng) [15]. In addition, this absorbent is designed to be used in thermal desorption system equipment. The adopted desorption parameters are presented in Table 1.

Pumping air into the tubes was carried out with a portable pump (AirChek, XR 5000) with sampling air flow fixed at 100 mL/min. It was, therefore, possible to adjust the sampling volume according to the safe sampling volume [15]. Sampling and preliminary analyses pointed out that the safe sampling volume for organic gases was 500 mL.

After sampling, the tubes were wrapped in tin foil and sent for analysis to the Environmental Technology Development Research Laboratory at the Chemistry Engineering College of Campinas State University (UNICAMP). Samples were analyzed using a *Perkin Elmer* gas chromatograph, model *AutoSystem XL*, equipped with a flame ionization detector (FID).

Table 1 Desorption parameters in automatic thermal desorption (ATD)

In order to separate the compounds, a 60-m long capillary column, 100% dimethyl polysiloxane, was used. The chromatographic conditions adopted in this study are presented in Table 2**.** The FID operational conditions were the following: temperature – 250 ºC; synthetic air flow – 420 mL/min; hydrogen flow – 45 mL/min.

Table 2 Chromatographic oven heating conditions

Quality control and calibration curves for organic gases

For quality control, organic emission tests included duplicate samplings (for all fuel blends and power loadings) and field blanks. Two tubes were used as field blanks, submitted to the same conditioning, storage and transport conditions as the tubes used in the analyses [15]. The detection and quantification limits (DL and QL) were estimated from the analytical response of laboratory blanks. The standard deviation of mass obtained in the blanks was multiplied by 3.3 to estimate the DL and by 10 to estimate the QL [16].

BTEX were quantified by external standard calibration. To prepare the solutions for the calibration curves, methanol (*Merck KGaA*) was used as a solvent. The stock solution preparation requires previous knowledge of the mass band of the substances that will be sampled. A six-point calibration curve (all points in triplicate) for each BTEX was performed so that these analytical curves covered a wide range of masses for the analytes in the samples. In all cases, the coefficients of determination (R^2) were greater than 0.99.

The concentration of each BTEX compound was determined considering its mass (as determined by chromatography) and the safe sampling volume used to trap the gas (500 mL). The retention times, detection and quantification limits for each BTEX are shown in Table 3**.**

Table 3 BTEX retention times, detection and quantification limits.

3. Results and discussion

3.1 Engine generator performance

The results obtained from engine performance parameters are presented in Table 4. A first important observation that can be drawn from the results is that mass consumption values were not statistically different from one another (at a 5% probability level), regardless of the applied load and fuel blend.

Table 4 - Mass consumption (Mc), brake specific fuel consumption (BSFC) and overall efficiency as a function of the system load (E) using diesel, biodiesel and their blends (at a 5% probability level)[a]

The results presented in Fig. 1 show that brake specific fuel consumption (BSFC) is not affected by variations in fuel blends, a pattern also observed by Oberweis and Al-Shemmeri[17] in their comparison of diesel, biodiesel and blends of the two. However, the increase in load supplied to the engine caused a statistically significant reduction in BSFC. Similar results were found by Silva et al. [14] when testing diesel and waste fat biodiesel in an engine generator identical to the one used in this study. Silva et al. [14] claim that the BSFC tends to be higher in low load situations (particularly when lower than 1.5 kW). Valente et al. [18] also observed that the BSFC tends to decrease with higher loads. According to Heywood [19], the increase in BSFC at lower loads is associated with low speeds, which cause lower inertial stress and reduce the mechanical efficiency. The latter is due to higher efforts to pump the gases inside and outside the combustion chamber, and to friction forces from mobile parts inside the engine. In addition to the preceding, Heywood [19] observed that when loads are increased, fuel mass consumption tends to increase due to the higher effort required. This higher amount of burnt fuel, supplies more energy inside the combustion chamber and, as a consequence, causes the temperature to increase. As a result, fuel is burned more efficiently because any residual that would be released with the exhaust gases, gets burned. Accordingly, despite the increase in fuel mass consumption, a reduction in BSFC with higher loads is observed due a more efficient thermodynamic use of the fuel [19].

Fig. 1 Brake specific fuel consumption (BSFC) as a function of fuel type, fuel blends and loads.

In Fig. 2, it can be observed that the tendency of the overall efficiency (E) was to increase for all types of blends, with higher efficiencies obtained when higher loadings were supplied to the engine. In addition, the overall efficiency increased with increasing content of biofuel in the mix. For SB, the gain in efficiency with increasing biofuel addition was marginal for the lower loads (0.5 and 1.0 kW; in fact there was a slight decrease for SB5). On the other hand, for the higher load (1.5 kW), the value of E actually decreased for soybean biofuels, but bounced up for the pure biofuel (SB100). The latter's overall efficiency was nearly 15% greater than that of B0 (14.4% from 12.7%). For BT, the general tendency was for E to increase with increasing loads and blends, with the exception of BT5 at 0.5 kW and BT20 at 1.5 kW. The maximum performance obtained in this study was 14.4%, for pure soybean diesel (SB100) at 1.5 kW load. The tendencies observed corroborate those obtained by Silva et al. [14], who also reached the conclusion that for loads lower than 1.5 kW, engine performances remained lower than 15%.

Fig. 2**.** Overall efficiency (E) as a function of system load and fuel type and blends.

3.2 Inorganic gas emissions - CO, SO_2 and NO_x

The concentrations of inorganic gas (CO, SO_2 and NO_x) emitted for each load, fuel type and blend are presented in Table 5. To simplify the interpretation of these results, they are also presented in graphic form in Fig. 3**.**

Table 5 Inorganic gas emissions (average values and standard deviation at a 5% probability level)[a]

Fig. 3. Inorganic gas emissions as a function of load, fuel type and blend.

Fig. 3a shows that CO emissions increased with small additions of biofuel to mineral diesel, regardless of the load applied. However, when biofuel additions became greater than 50%, CO emissions decreased abruptly and significantly. Beef tallow biodiesel led to greater decreases in CO emissions than soybean biodiesel. These results were similar to those presented by U.S. EPA [1] which concluded that animal fat biodiesel, due to its higher level of molecule saturation, led to greater reductions in CO emissions than the soybean biodiesel.

Reductions in CO emissions were higher in conditions in which higher load was applied to the engine. This tendency was also observed by Bueno[20], who evaluated CO combustion emissions in an engine fueled with diesel and 20% soybean ethyl ester (B20), working at constant speed (2000 rpm) and under load fractions 33, 66 and 100% of maximum torque. In general, the CO emissions presented herein corroborate those found in the technical literature [4, 21-23].

The percentage of oxygen measured (Table 5) was lower for blends with low biofuel additions (SB5, BT5, SB20 and BT20), which is associated with the greater CO emissions observed for these blends (Fig. 3a**)**. As more biofuel is added to mineral diesel, the concentrations of emitted O_2 increase and those of CO become lower. Schumacher et al. [24] and Wang et al. [25] explained that the presence of oxygen in biodiesel provides better conditions for complete combustion, leading to a reduction in CO emissions. In addition, biodiesels have higher cetane numbers, which facilitates complete combustion (as it promotes reduction in ignition delay) and, consequently leads to lower CO release [26, 27].

For SB5, the results showed a slight increase in SO_2 emissions at higher loads, while the emissions at the lowest load remained the same. For beef tallow, however, SO_2 emissions remained at almost the same level for the lower loads after an addition of 5% of this biofuel, but decreased by nearly 25% when the higher load (1.5 kW) was applied.

For blends with more than 20% of the two biofuels, the trend in SO_2 emissions was quite similar to that observed for CO, i.e. a continuous decrease in emissions with further addition of the biofuels. BT emissions for all loads – and blends with more than 20% of biofuels - were lower than those of SB, except when pure biodiesel was employed. The fact that BT blends generate fewer SO_2 emissions, agrees with the findings of a study by Miller [28], who observed that the emissions level of this pollutant are lower with animal fat biodiesel, when compared to soybean biodiesel.

In the end, SO_2 emissions from each of the pure biofuels were approximately 75% lower than those from pure diesel (B0). Miranda[29] reached similar results employing waste cooking oil biodiesel. Reductions found for this pollutant are justified by the fact that the biodiesel is practically sulfur free [27, 30-32] compared to 1800 ppm commonly found in diesel.

NO_x emissions showed a very different pattern when compared to the other two pollutants discussed above. The emissions of this pollutant remarkably increased with increasing loads applied to the engine, a behavior also observed by Cheung et al.[33], Elango and Senthilkumar [34], and Xue et al. [35]. However, considering each load separately, there is no apparent pattern associated with NO_x emissions as the amount of biofuel in the mix increases. A greater database might help identify a clearer response of the system to the increase in biofuel addition.

Nabi et al. [21] pointed out that the highest oxygen content in biodiesel [due to a higher concentration of oxygenated groups, such as esters] and proper adjustment of fuel injection timing can contribute to the increase in NO and NO_2 emissions. Other studies (i.e. Oberweis and Al-Shemmeri [17]) claim that the increase in NO_x emissions with the increase in load, results from the higher temperatures reached in the combustion chamber (and NO_x emissions are directly related to the gas combustion temperature). In the present study, the increases in temperature (data not presented) from the low to the mid loadings are minimum, whereas the increases from the mid to the high load vary between 5^o C and 10^o C (by all means, not a steep increase).

Li and Gülder [36] claim that the increase in the biodiesel cetane number might be responsible for a reduction in NO_x emissions under low loading conditions. Considering that the loads employed in this study were 10%, 20% and 30% of the maximum load, the previous statement seems to corroborate the findings of the present study.

3.3 Organic Gas Emissions – BTEX

BTEX Determination

The average concentrations obtained as a function of the engine load and fuel used, for the four compounds, are illustrated in Figures 4 to 7. Analyses of the field blanks prepared for each blend and loading did not show the presence of any of the BTEX compounds within detectable limits.

Fig. 4. Benzene emissions with different fuels and loads evaluated.

Fig. 5**.** Toluene emissions with different fuels and loads evaluated.

Fig. 6. Ethylbenzene emissions with different fuels and loads evaluated.

Fig. 7. Xylene emissions with different fuels and loads evaluated.

The general pattern for all four compounds was clearly of decreasing emissions with increasing addition of both biofuels. However, the magnitude and intensity of the decrease in emissions varied depending on the type of compound and loading applied. Table 6 summarizes the changes in BTEX concentrations for all blends and loads.

Table 6 BTEX emissions relative to pure diesel (SB0 or BT0)

One of the most common arguments in the literature to explain the BTEX emission reductions when biodiesel is used as a substitute for diesel is the higher oxygen content and cetane number of biodiesels. The fact that biodiesels are more oxygenated than pure diesel favors their oxidation, therefore leading to lower emissions of these pollutants. A higher cetane number favors combustion and promotes lower ignition delay, which reduces incomplete burning, and, consequently, emission of these hydrocarbons [37, 38].

Soybean presented higher BTEX concentrations than beef tallow for all comparable blends and loadings. This possibly results from the higher cetane index of methyl esters originated from the beef tallow biodiesel, which possess a higher degree of molecule saturation [27, 39]. The lowest emissions were found when pure beef tallow (BT100) was used. SB100 produced lower BTEX emissions than those of pure diesel, except in the case of Benzene, for which SB100-associated emissions were higher when the lower and higher loadings were applied. The higher oxygen content of pure biodiesel – as compared to pure diesel – also explains why these compounds are more easily oxidized, and, as a result, their use leads to lower emission values than pure diesel [23].

In the case of benzene, there was a reduction in emissions with increasing loads applied to the engine (Fig. 4) for blends containing 50% of the two biofuels (i.e. SB50 and BT50). This fact was also reported by Di et al. [38] and Cheung et al. [33] and can be attributed to the higher temperatures reached inside the combustion chamber at higher loads, which facilitates thermal oxidation of benzene. For BT100, there was a slight increase in emissions from the lower loading to the intermediate one (Fig. 4).

Ballesteros et al. [40] , who tested the response of a diesel engine when biodiesels were employed, observed that the only monoaromatic detected in exhaust, for blends with over 70% of biofuels, was benzene.

As far as Toluene emissions are concerned, only the SB50 blend (for all loadings) did not follow the general pattern of decreasing emissions with addition of SB biofuel to pure diesel.

An addition of 50% soybean biofuel to pure diesel led to an increase in ethylbenzene emissions for the intermediate and higher loadings. Otherwise, the general pattern of decreasing emissions with addition of biofuel and increase in loading observed for this compound, corroborate what was found in several studies, including one by the U.S. EPA [1], which concluded that ethylbenzene emission reductions could be greater than 61% when biodiesel is used as a substitute for diesel. In another study, Miranda [29] found that ethylbenzene emissions were approximately 75% lower when biodiesel was used, while Magara-Gomez et al. [41] obtained nearly no ethylbenzene emissions when using soybean biodiesel and beef tallow biodiesel in a farm tractor.

Finally, as far as xylenes are concerned, the increase in emissions associated with SB50 was only noticeable for the intermediate and higher loadings (1.0 and 1.5 kW), although much less steep than observed for the other compounds. Several other studies observed a clear reduction in xylene emissions when biodiesels were added to pure diesel [1, 33, 38, 41].

According to Corrêa and Arbilla [3], in order to explain emission variations with the addition of biodiesel to diesel, it is necessary to analyze in detail the engineering of the engine generator employed, as well as the degradation mechanisms of organic compounds at high combustion temperatures (thermodynamic destruction, direct emission through incomplete combustion and pyrosynthesis). The same authors also highlighted that the diesel cycle engine combustion is a complex process influenced by several factors such as liquid atomization, quantity of air in the mixture and burning at high temperatures and pressures. The addition of biodiesel to diesel might alter some of the latter's physico-chemical properties and this might result in greater or lower amounts of substances released to the atmosphere.

4. Conclusions

The present study involved two precursors of biodiesel, namely soybean and beef tallow. Together, they are responsible for approximately 92% of biodiesel production in Brazil. The results permit to conclude that the use of the two selected biodiesels is advantageous with respect to performance and combustion emissions for the engine generator tested.

A first important observation that can be drawn from the study is that mass consumption values did not vary significantly, regardless of the biofuel, applied load and fuel blend. Brake specific fuel consumption is not affected by variations in fuel blends for both types of biofuels. The tendency of the overall efficiency was to increase for all types of blends when higher loadings were supplied to the engine. In addition, the overall efficiency increased with increasing content of biofuel in the mix.

As far as emissions abatement is concerned, reductions were in fact obtained, but their magnitude – or importance – varied according to the contaminant studied and to the operational conditions. Indeed, there were reductions in CO, SO_2 and BTEX emissions with the use of biodiesel. Beef tallow biodiesel led to greater decreases in CO emissions than soybean biodiesel. The same applied to SO_2 reductions, except when pure biodiesel was employed. In the latter case, emissions from the pure biodiesels were approximately the same. This situation was expected, considering that these fuels are basically aromatic and sulfur free in their composition. Use of beef tallow biodiesel led to lower emissions than those produced by soybean biodiesel. NOx emissions showed a very different pattern when compared to the other two pollutants with emissions notably increasing with increasing loads. No particular pattern in NOx emissions reduction or increase as a function of mix increase was observed.

It should be pointed out that the best performance and emission reductions for the engine generator tested occurred when each of the two biodiesels used were blends containing greater than 50% of the two biofuels. Therefore, considering the methodology followed in this study, the use of the current proportion of biodiesel addition to diesel in Brazil (7%) does not present an optimal environmental advantage.

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References

[1] USEPA (2002). A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions, Report EPA420-P-02-001, National Vehicle and Fuel Emissions Laboratory, Ann Arbor, MI, 126 p.

[2] Ferreira, S.L., et al. (2008). *Analysis of the emissions of volatile organic compounds from the compression ignition engine fueled by diesel-biodiesel blend and diesel oil using gas chromatography.* Energy, 33(12): 1801-6.

[3] Corrêa, S.M. and G. Arbilla (2006). *Aromatic hydrocarbon emissions in diesel and biodiesel exhaust.* Atmospheric Environment, 40(35): 6821-6826.

[4] Dorado, M.P., et al. (2003). *Exhaust emissions from a diesel engine fueled with transesterified waste olive oil.* Fuel, 82(11): 1311-1315.

[5] Buczynska, A.J., et al. (2009). *Atmospheric BTEX-concentrations in an area with intensive street traffic.* Atmospheric Environment, 43(2): 311-318.

[6] Fernandes, M.B., et al. (2002). *Atmospheric BTX and polyaromatic hydrocarbons in Rio de Janeiro, Brazil.* Chemosphere, 47(4): 417-425.

[7] Ras-Mallorqui, M.R., R.M. Marce-Recasens, and F. Borrull-Ballarin (2007). *Determination of volatile organic compounds in urban and industrial air from Tarragona by thermal desorption and gas chromatography-mass spectrometry.* Talanta, 72(3): 941-950.

[8] Muezzinoglu, A., M. Odabasi, and L. Onat (2001). *Volatile organic compounds in the air of Izmir, Turkey.* Atmospheric Environment, 35(4): 753-760.

[9] Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP). Boletim Mensal de Biodiesel, November 2013, Brasília - DF, 14 p.

[10] Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP). Resolução No. 14, May 2012, Brasilia, 9 p.

[11] Corrêa, I.M., J.V.G. Maziero, and M. Storino (2011). *Mistura de biodiesel de sebo bovino em motor diesel durante 600 horas.* Ciência Rural, 41(7): 1189-1194.

[12] Penido Filho, P., *Os motores à combustão interna*. 1st ed. Vol. 1. 1983, Belo Horizonte: Ed. Lemi. 699 p.

[13] Ministério de Minas e Energia (MME). C.N.d.P. Energética. Resolução nº 06, Art. 2º, Lei nº 11.097/2005, 2009, Brasília, Brazil.

[14] Silva, M.J., et al. (2012). *Motor gerador ciclo diesel sob cinco proporções de diesel com óleo diesel.* Revista Brasileira Engenharia Agrícola e Ambiental, 16(3): 320-326.

[15] USEPA (1999). Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (TO-17), 2nd ed., Report EPA/625/R-96/010b, USEPA, Cincinnati, OH, 53 p.

[16] Ribani, M., C.H. Collins, and C.B.G. Bottoli (2007). *Validation of chromatographic methods: Evaluation of detection and quantification limits in the determination of impurities in omeprazole.* Journal of Chromatography A, 1156(1–2): 201-205.

[17] Oberweis, S. and T.T. Al-Shemmeri (2010). *Effect of Biodiesel blending on emissions and efficiency in a stationary diesel engine*. in *10th Intl. Conf. on Renewable Energies and Power Quality*, (Ed.), Granada, Spain, 23-25 March 2010, CD-Rom, Paper 314.

[18] Valente, O.S., et al. (2010). *Fuel consumption and emissions from a diesel power generator fuelled with castor oil and soybean biodiesel.* Fuel, 89(12): 3637-3642.

[19] Heywood, J.B., *Internal combustion engine fundamentals*. 1988, New York: McGraw Hill. 930 p.

[20] Bueno, A.V. (2006). *Análise da operação de motores diesel com misturas parciais de biodiesel.* Ph.D. Thesis, Faculdade de Engenharia Mecânica, Universidade Estadual de Campinas; 120 p.

[21] Nabi, M.N., M.M. Rahman, and M.S. Akhter (2009). *Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions.* Applied Thermal Engineering, 29(11-12): 2265-2270.

[22] Pereira, R.G., et al. (2007). *Exhaust emissions and electric energy generation in a stationary engine using blends of diesel and soybean biodiesel.* Renewable Energy, 32(14): 2453-2460.

[23] Qi, D.H., et al. (2009). *Combustion and performance evaluation of a diesel engine fueled with biodiesel produced from soybean crude oil.* Renewable Energy, 34(12): 2706-2713.

[24] Schumacher, L.G., et al. (1996). *Heavy-duty engine exhaust emission tests using methyl ester soybean oil/diesel fuel blends.* Bioresource Technology, 57(1): 31-36.

[25] Wang, W.G., et al. (2000). *Emissions from nine heavy trucks fueled by diesel and biodiesel blend without engine modification.* Environmental Science and Technology, 34(6): 933-939.

[26] Altiparmak, D., et al. (2007). *Alternative fuel properties of tall oil fatty acid methyl ester-diesel fuel blends.* Bioresource Technology, 98(2): 241-246.

[27] Knothe, G., et al., *Manual do Biodiesel*. 2006, São Paulo: Edgard-Blücherp.

[28] Miller, C.A. (2008). Characterizing Emissions from the Combustion of Biofuels, Report EPA/600/R-08/069, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC, 51 p.

[29] Miranda, G.R. (2007). *Avaliação das Emissões Atmosféricas Provenientes da Combustão do Diesel, Biodiesel de Óleo de Fritura e suas Misturas.* M.Sc. Thesis, Universidade Federal de Santa Catarina; 108 p.

[30] Agarwal, A.K. (2006). *Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines.* Prog. Energy Combust. Sci., 33: 233-271.

[31] Tashtoush, G.M., M.I. Al-Widyan, and M.M. Al-Jarrah (2004). *Experimental study on evaluation and optimization of conversion of waste animal fat into biodiesel.* Energy Conversion and Management, 45(17): 2697-2711.

[32] Villarreyes, J.A.M., et al. (2007). *Diesel/biodiesel proportion for by-compression ignition engines.* Fuel, 86: 1977-1982.

[33] Cheung, C.S., L. Zhu, and Z. Huang (2009). *Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol.* Atmos. Environ., 43: 4865-4872.

[34] Elango, T. and T. Senthilkumar (2011). *Combustion and emission characteristics of a diesel engine fuelled with jatropha and diesel oil blends.* Therm. Sci., 15(04): 1205-1214.

[35] Xue, J., T.E. Grift, and A.C. Hansen (2011). *Effect of biodiesel on engine performances and emissions.* Renew. Sust. Energ. Rev., 15: 1098-1116.

[36] Li, X. and Ö. Gülder, L., *Effects of fuel cetane number , density and aromatic content on diesel engine NOx emissions at different operating conditions*, in *4th International Symposium Comodia*. 1998: Kyoto, Japan. p. 111-116.

[37] Lim, Y., et al. (2012). *The Effect of the Diesel Cetane Number on Exhaust Emissions Characteristics by Various Additives.* J. Therm. Sci. Techn., 7(01): 90-103.

[38] Di, Y., C.S. Cheung, and Z. Huang (2009). *Experimental investigation on regulated and unregulated emissions of a diesel engine fueled with ultra-low sulfur diesel fuel blended with biodiesel from waste cooking oil.* Sci. Total Environ., 407: 835-846.

[39] Dabdoub, M.J., J.L. Bronzel, and M.A. Rampin (2009). *Biodiesel: Visão Crítica do Status Atual e Perspectivas na Academia e na Indústria.* Revista Química Nova, 32(03): 776-792.

[40] Ballesteros, R., et al. (2008). *Speciation of the semivolatile hydrocarbon engine emissions from sunflower biodiesel.* Fuel, 87(10-11): 1835-1843.

[41] Magara-Gomez, K.T., et al. (2012). *Sensitivity of hazardous air pollutant emissions to the combustion of blends of petroleum diesel and biodiesel fuel.* Atmos. Environ., 50: 307-313.

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Table 1. Desorption parameters in automatic thermal desorption (ATD)

Parameter	ATD operation condition
Valve temperature (ºC)	205
Tube temperature (ºC)	300
Trap high (ºC)	300
Trap low (ºC)	-30
Transfer line (ºC)	205
Desorption time (min)	15
Desorption flow (mL/min)	60
Column flow (mL/min)	1
Inletsplit (mL/min)	45
Outletsplit (mL/min)	25
Pressure (psi)	20
Carrier gas	He

Table 2. Chromatographic oven heating conditions

Step	Rate (ºC/min)	Temperature (ºC)	Time (min)
Initial	0.0	35	35
1	2.0	60	10
2	1.5	80	5
3	7.0	100	10

Table 3. BTEX retention times, detection and quantification limits.

Pollutant	Retention time (min)	Detection limit (ng)	Quantification limit (ng)
Benzene	12.82	2.43	8.10
Toluene	22.10	11.67	38.91
Ethylbenzene	33.30	3.22	10.74
m.p-Xylenes	35.87	0.06	0.20
o-Xylene	38.51	0.19	0.64

Table 4. Mass consumption (Mc), break specific fuel consumption (BSFC) and overall efficiency as a function of the system load (E) using diesel, biodiesel and their blends (at 5% probability level)[a]

Parameters	Load (kW)	Fuel									
		B0	SB 5	BT 5	SB 20	BT 20	SB 50	BT 50	SB 100	BT 100	LA[b]
MC (g/s)	0.5	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.2a
	1.0	0.2	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.3	0.3a
	1.5	0.2	0.3	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.3a
	AVG[c]	0.2a	0.3a	0.3a	0.3a	0.2a	0.3a	0.3a	0.3a	0.3a	
BSFC (g/kWh)	0.5	2282.3 ±196.3	2847.2 ±772.7	2444.5 ±94.3	2209.3 ±105.6	2009.3 ±18.3	2315.0 ±325.4	1990.0 ±196.7	2602.3 ±325.8	1943.1 ±112.5	2293.7a
	1.0	1079.4 ±9.9	1177.5 ±72.0	1026.8 ±19.3	1091.9 ±111.4	931.7 ±6.0	1080.7 ±71.5	1083.3 ±31.4	1070.8 ±48.8	1066.0 ±207.9	1067.6b
	1.5	688.5 ±15.6	750.3 ±28.6	679.0 ±3.8	767.5 ±140.0	728.6 ±114.3	720.9 ±37.4	697.3 ±60.3	691.9 ±45.9	708.4 ±47.8	714.7c
	AVG	1350.1a	1591.7a	1383.4a	1356.2a	1223.2a	1372.2a	1256.9a	1454.9a	1239.2a	
E (%)	0.5	3.8 ±0.3	3.2 ±0.9	3.5 ±0.1	4.1 ±0.2	4.4 ±0.0	4.1 ±0.6	4.7 ±0.5	3.9 ±0.5	5.1 ±0.3	4.1c
	1.0	8.0 ±0.1	7.4 ±0.5	8.4 ±0.2	8.3 ±0.8	9.5 ±0.1	8.6 ±0.6	8.6 ±0.3	9.3 ±0.4	9.5 ±1.9	8.6b
	1.5	12.6 ±0.3	11.6 ±0.4	12.7 ±0.1	11.9 ±2.2	12.3 ±1.9	12.9 ±0.7	13.4 ±1.2	14.4 ±1.0	14.0 ±0.1	12.9a
	AVG	8.1ab	7.4b	8.2ab	8.1ab	8.8ab	8.5ab	8.9ab	9.2a	9.6a	

[a] The averages followed by the same letter are not statistically different from one another.
[b] LA: load average
[c] AVG: average

Table 5. Inorganic gas emission (average values and standard deviation at 5% probability level)[a]

Parameters	Load (kW)	Fuel									
		B0	SB 5	BT 5	SB 20	BT 20	SB 50	BT 50	SB 100	BT 100	LA[b]
CO (ppm)	0.5	1506.1 ± 282.2	1809.7 ± 157.5	2149.2 ± 155.9	2104.0 ± 142.3	1619.9 ± 212.2	1780.5 ± 260.3	800.0 ± 138.7	788.0 ± 216.9	533.4 ± 150.6	1454.5 a
	1.0	1252.3 ± 231.5	1605,0 ± 170.9	1415.5 ± 131.3	1521.2 ± 208.3	1073.1 ± 98.9	1376.7 ± 238.2	546.7 ± 171.3	568.6 ± 169.8	427.3 ± 98.9	1087.4 b
	1.5	988.8 ± 274.1	1189.2 ± 112.3	1041.8 ± 56.0	1043.9 ± 68.0	672.9 ± 56.0	920.1 ± 150.7	442.6 ± 74.8	530.0 ± 204.8	334.7 ± 73.7	796.0 c
	AVG[c]	1249.1 ab	1534.6 ab	1535.5 ab	1556.4 a	1122.0 b	1359.1 ab	596.5 c	628.9 c	431.8 c	
SO_2 (ppm)	0.5	65.9 ± 6.3	61.7 ± 6.0	71.4 ± 5.3	67.1 ± 2.4	42.0 ± 10.2	40.8 ± 6.1	15.8 ± 2.8	18.2 ± 6.8	12.9 ± 1.2	44.0 a
	1.0	48.3 ± 6.3	55.2 ± 4.7	49.5 ± 1.9	51.0 ± 0.5	22.7 ± 0.6	30.4 ± 3.0	10.6 ± 2.1	13.0 ± 2.0	11.3 ± 0.7	32.4 b
	1.5	42.6 ± 2.6	46.2 ± 0.6	31.8 ± 0.3	23.8 ± 3.1	12.9 ± 1.0	14.8 ± 0.5	6.2 ± 2.2	8.6 ± 0.5	10.0 ± 0.2	21.9 c
	AVG	52.3 a	54.4 a	50.9 a	47.3 a	25.9 bc	28.7 b	10.9 c	13.2 bc	11.4 c	
NO_x (ppm)	0.5	24.1 ± 5.3	29.2 ± 2.5	32.3 ± 2.2	35.9 ± 1.2	36.0 ± 4.9	31.7 ± 1.6	46.4 ± 10.7	36.9 ± 3.8	52.7 ± 6.7	36.1 c
	1.0	38.3 ± 13.4	43.3 ± 4.8	51.1 ± 9.8	55.4 ± 9.3	52.0 ± 15.7	52.5 ± 9.4	45.0 ± 12.9	29.7 ± 13.1	67.3 ± 6.5	48.3 b
	1.5	91.1 ± 24.5	86.1 ± 23.7	92.1 ± 14.1	93.5 ± 17.0	94.1 ± 4.3	65.7 ± 19.1	77.7 ± 13.9	88.4 ± 36.5	88.6 ± 7.2	86.4 a
	AVG	51.2 a	52.9 a	58.5 a	61.6 a	60.7 a	50.0 a	56.4 a	51.7 a	69.5 a	
O_2 (%)	0.5	17.8 ± 0.7	17.3 ± 0.5	17.1 ± 0.4	17.0 ± 0.1	17.4 ± 0.5	17.6 ± 0.7	18.4 ± 0.5	18.5 ± 0.6	18.4 ± 0.7	17.7 a
	1.0	18.0 ± 0.7	17.1 ± 0.7	16.8 ± 0.6	16.5 ± 0.6	17.3 ± 0.5	17.3 ± 0.8	18.7 ± 0.5	19.1 ± 0.6	18.3 ± 0.6	17.7 a
	1.5	17.0 ± 0.4	16.5 ± 0.6	16.2 ± 0.5	16.1 ± 0.5	17.1 ± 0.4	17.6 ± 0.7	18.2 ± 0.5	18.4 ± 1.1	18.0 ± 0.5	17.2 b
	AVG	17.6 b	17.0 cde	16.7 de	15.5 e	17.3 bcd	17.5 bc	18.4 a	18.6 a	18.2 a	

[a] Averages followed by the same letter are not statistically different from one another.
[b] LA: load average
[c] AVG: average

Table 6. BTEX emissions relative to pure diesel (SB0 or BT0)

Fuel	Load (kW)	Difference relative to pure diesel (%)			
		Benzene	Toluene	Ethylbenzene	Xylene
SB 50	0.5	> 100.0	+23.4	-52.9	-68.2
BT 50	0.5	-29.4	-39.5	-77.7	-75.9
SB 100	0.5	+19.5	-78.4	-92.5	-94.9
BT 100	0.5	-82.9	-92.7	-96.4	+98.0
SB 50	1.0	+65.2	+20.5	+17.1	+25.8
BT 50	1.0	-59.0	-48.9	-65.2	-31.8
SB 100	1.0	-29.5	-79.9	-82.8	-84.7
BT 100	1.0	-72.5	-90.3	-91.9	-90.0
SB 50	1.5	> 100.0	+88.9	+64.9	+27.7
BT 50	1.5	-20.5	-39.8	-71.5	-57.4
SB 100	1.5	> 100.0	-40.8	-65.1	-80.9
BT 100	1.5	-27.3	-72.4	-80.6	-88.9

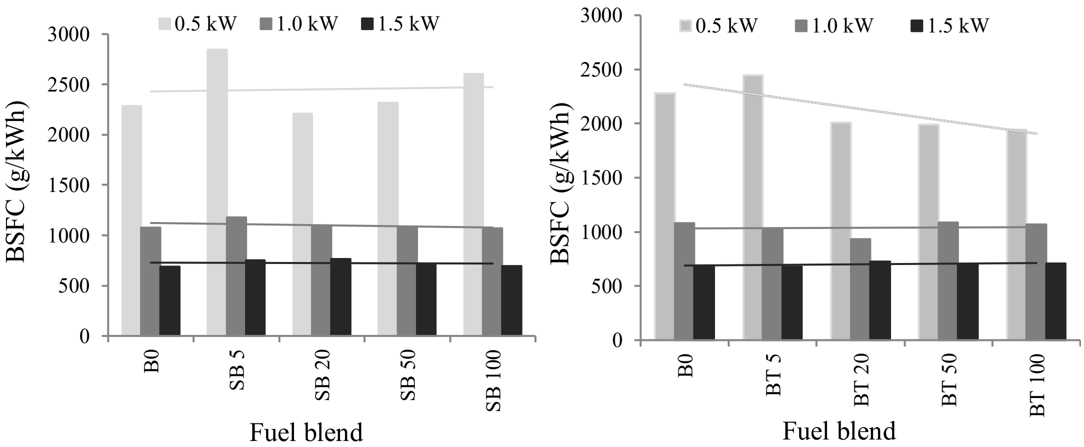

Figure 1. Break specific fuel consumption (BSFC) as a function of fuel type, fuel blends and loads.

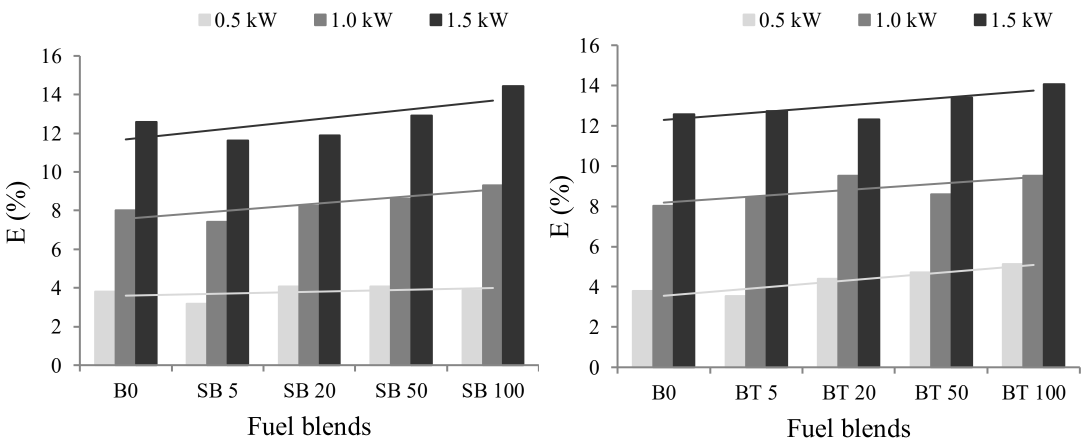

Figure 2. Overall efficiency (E) as a function of system load and fuel type and blends

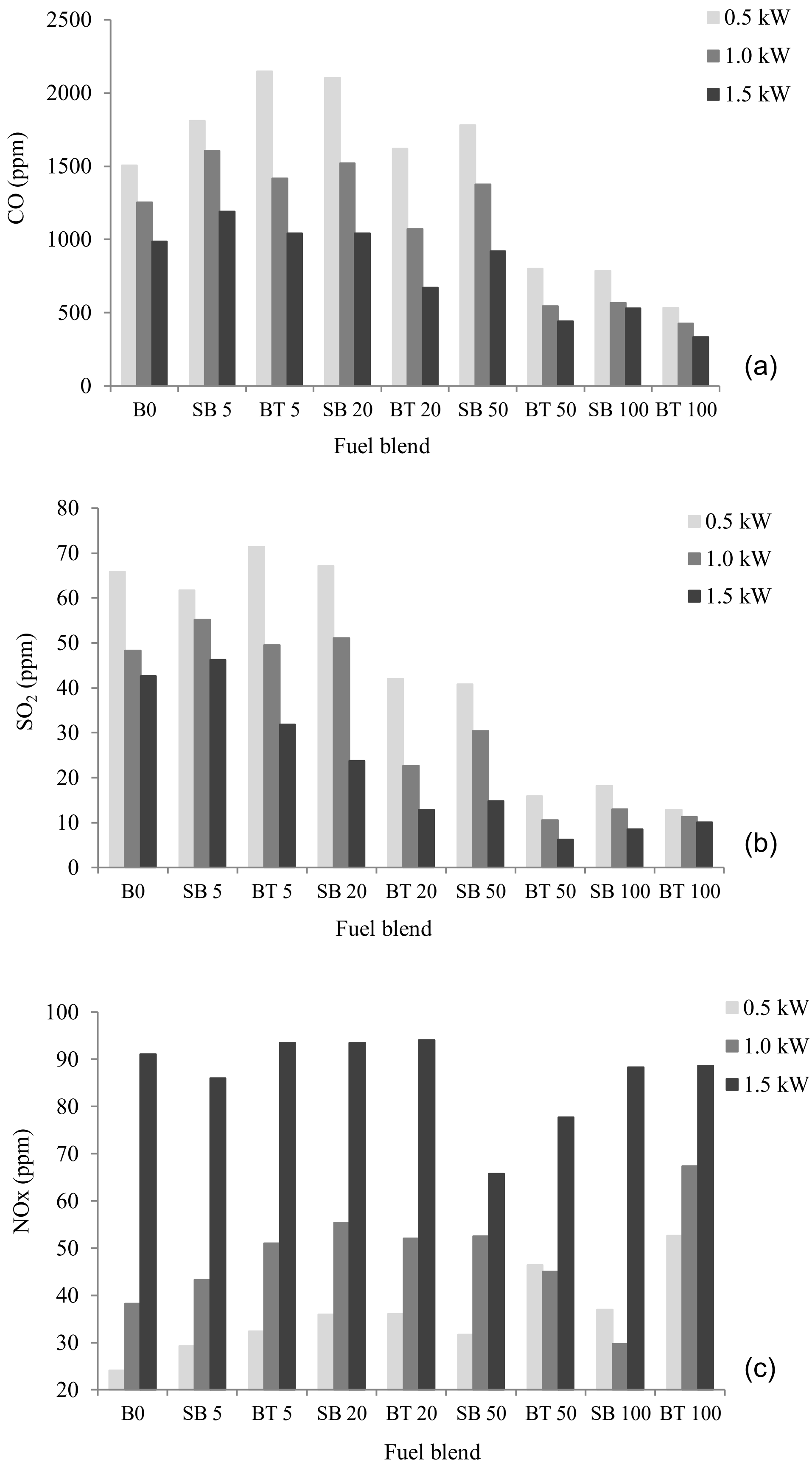

Figure 3. Inorganic gas emissions as a function of load, fuel type and blends.

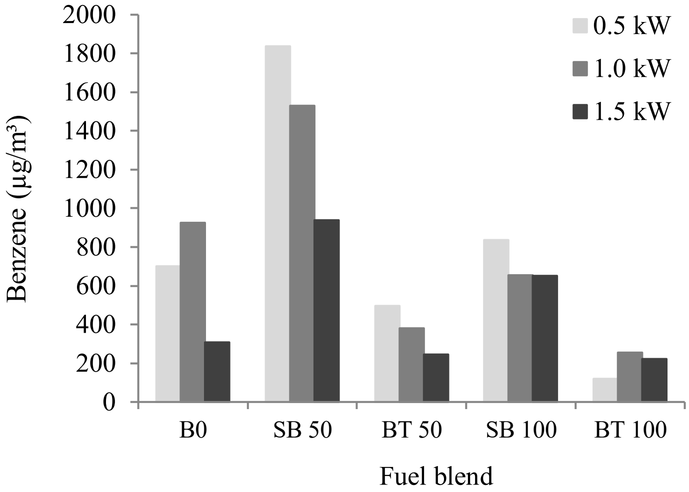

Figure 4. Benzene emissions with different fuels and loads evaluated.

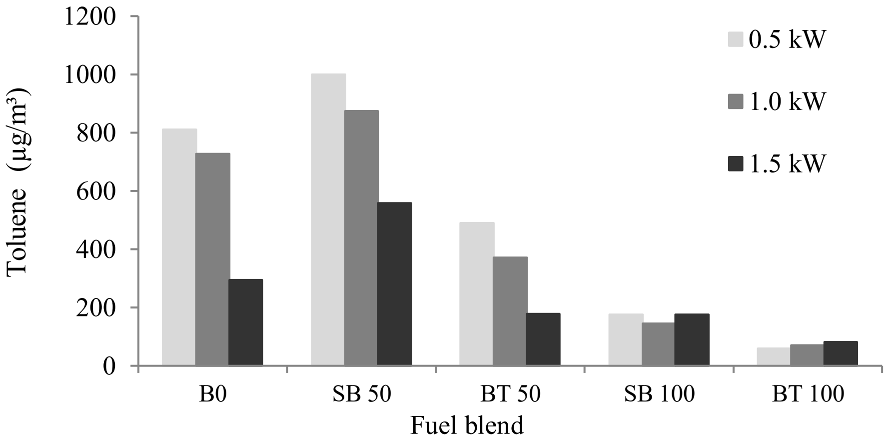

Figure 5. Toluene emissions with different fuels and loads evaluated.

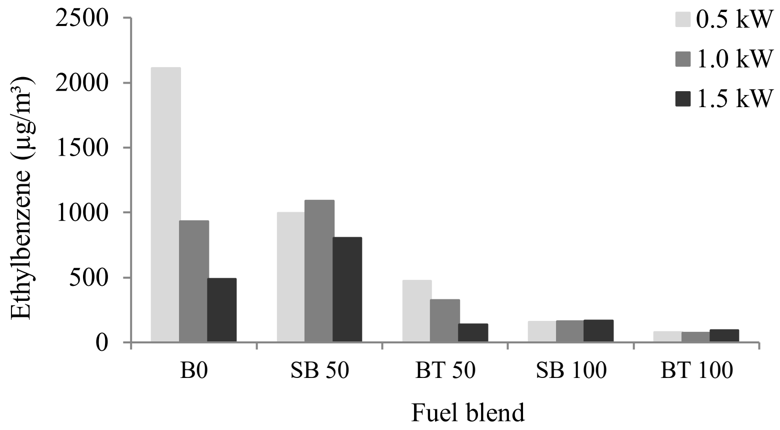

Figure 6. Ethylbenzene emissions with different fuels and loads evaluated.

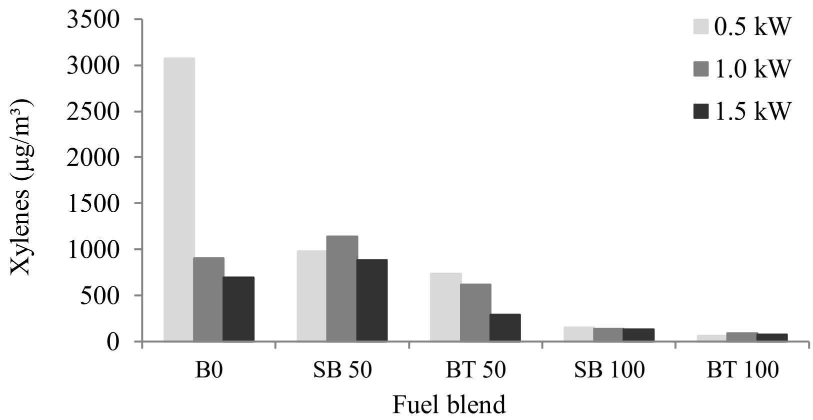

Figure 7. Xylenes emissions with different fuels and loads evaluated.